

Design of thermochemical biorefineries: Experience of Bioenergy Group of University of Seville

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FECUNDUS Summer School CIEMAT, Madrid, Spain July 6th 2012

Fecundus Summer School, CIEMAT, Madrid, 3-6 July 2012



- 1. The design problem of biorefineries
- 2. Thermochemical production of ethanol



 Chemicals and fuels can be produced from thermochemical conversion of biomass





There are many routes to produce fuels and chemicals from syngas



Adapted from "Preliminary Screening — Technical and EconomicAssessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas" P.L. Spath and D.C. Dayton. NREL, 2005

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General scheme of a biorefinery based on biomass gasification







General comments

- In a thermochemical biorefinery multiple targets products are generated (**polygeneration**)
- Multiple biomass feedstocks may solve biomass supply logistics (seasonal dependence of biomass)
- **Coal and natural gas** may be also used as secondary (cheaper) feedstocks at the expense of larger GHG emission





The synthesis and design of a thermochemical biorefinery is challenging:

- The objective is to find the **most profitable process** for chosen target products but.....
- Many possible plant configurations depending on choices of technologies for gasification, gas cleaning, etc
- Process integration must be also addressed:
 - Heat recovery (design of heat exchanger network)
 - Utility system (steam network and power cycle design)
- Environmental constraints may exist (a minimum reduction of GHG emission is required to biofuels)



Process superstructure for DME, MeOH and FT production

From "Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis".Laurence Tock, Martin Gassner, Francois Maréchal. Biomass and Bioenergy, 34 (2010)1838–1854

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The problem is complex:

- Many degrees of freedom
- Environmental constraints

 Uncertainty in the performance of immature technologies or mature technologies under non-conventional process conditions

A systematic approach better be followed to address the design problem





Systematic approach for process design





Let's see the design problem for the case of thermochemical production of ethanol

The following work has been funded by Abengoa Bioenergia and the Spanish Ministry of Science and Innovation under "I+DEA" CENIT project



Syngas can be converted into ethanol and other alcohols (Higher Alcohol Synthesis, HAS) over mixed alcohols catalysts:





Our objective is to find the most profitable process for producing ethanol considering the following options in critical areas:

-Two gasification technologies (entrained flow gasifier, dual fluidized bed gasifier)

- **Two types of mixed alcohols catalysts** (molybdenum sulfide catalyst, Rh-based catalyst).

- Three reforming technologies (steam reforming, autothermal reforming, partial oxidation)

- **Two tar removal technologies** (oil scrubbing, tar reforming) only if DFB gasifier is chosen



 For each sound combination a process configuration was created









Process configurations for options EFG-ATR-S₂Mo and EFG-ATR-Rh

From "Technoeconomic assessment of ethanol production via thermochemical conversion of biomass by entrained flow gasification". A.L. Villanueva Perales, C. Reyes Valle, P. Ollero, A. Gómez-Barea. Energy, 36, (2011) 4097-4108.





Process configurations for options DFBG-S₂Mo-Oil Scrub. and ATR or SMR

From "Techno-economic assessment of biomass-to-ethanol by indirect fluidized bed gasification: impact of reforming technologies and comparison with entrained flow gasification". Carmen Reyes Valle; Angel L Villanueva Perales; Pedro Ollero; Alberto Gómez-Barea. Submitted to Fuel Journal.

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Modelling and simulation

- Each process configuration was modelled in Aspen Plus chemical process simulator
- Process units were modelled using simple models based on experimental data.
- Heat integration was made inspecting the heat offers and demands along the plant and selecting proper matches between streams.
- The plant was designed to be energy self-sufficient (no electricity import/export)



Modelling of gasifiers (*)

(1) Entrained Flow Gasifier: Chemical equilibrium is assumed due to high operating temperature (>1200 °C)



Conceptual modelling

Modelling in Aspen Plus

(*) "Guidelines for selection of gasifiers modelling strategies". Ángel L. Villanueva Perales, Alberto Gómez Barea, Enrique Revuelta, Manuel Campoy, Pedro Ollero. Proceedings of 16th European Biomass Bonference & Exhibition, 980-986, 2008



(2) Dual fluidized bed gasifier:





(2) Dual fluidized bed gasifier:

- Modelling based on the work of Spath et al. (*)

-Correlations of product mass yields (light gases, tars, char) as function of temperature from experiments with different woody biomass

- Correction of mass yields to fulfill atom balances

- Adjustment of gasification bed temperature or natural gas supply to combustor in order to fulfill heat balance

^{(*) &}quot;Biomass to Hydrogen Production and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier". P. Spath, A. Aden, T. Eggeman, M. Ringer, B. Wallace, and J. Jechura. NREL, 2005.



(2) Dual fluidized bed gasifier:



Modelling of dual fluidized bed gasifier in Aspen Plus



Modelling of reformers

- ATR and POX units assumed at chemical equilibrium due to high operating temperature (>1000 °C)
- Uncertainty in performance of SMR due to nonconventional operating conditions:
 - Syngas with low CH₄ content as feed to reformer
 - High CO₂/CH₄ ratio
- Lab scale experiments with commercial reforming catalyts to determine performance at such operating conditions
- Modelling of SMR with temperature approach to equilibrium in order to match experimental performance

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X CH4

— X CO2 Eq (T-30)



Modelling of SMR reformer (*)



High pressure fixedbed lab reactor Actual and predicted performance with 30 °C approach to chemical equilibrium. Effect of operating temperature. 18 bar, S/C = 3.5, %CH₄ = 8 70 2.0 60 1.8 50 (%) Conversion Ratio H₂/CO 1.6 40 30 1.4 20 1.2 10 1.0 0 870 890 910 T(°C)

(*) "Characterization of a steam methane reforming catalyst with recirculation gas from an ethanol synthesis reactor" M. Hernández et al. ANQUE International Congress of Chemical Engineering ,2012, Seville

X CH4 Eq (T-30)

-H2/CO real

X CO2

→ H2/CO eq (T-30)



Modelling of other process units

• <u>Ethanol synthesis reactor</u>: Modelled based on experimental performance of mixed alcohols catalyst in the lab.

- Added complexity of a kinetic model is not worthwhile at the first stage of design.



The point is....

Use models as simple as possible to get meaningful results, but no simpler



Economic analysis

- A plant size of 500 MWth (HHV) biomass input is chosen

-Results of the simulations are used to calculate operating and capital costs

- Capital costs of commercial units are not usually available in literature: contact with technology suppliers and engineering companies whenever possible

- Cash flow analysis is carried to calculate a minimum ethanol selling price to achieve desired rate of return.

- Sensitivity analysis to assess uncertainty in capital costs and biomass price



Summary

-Design of biorefineries, like any other chemical process, is a complex problem

- Additional complexities due to environmental constraints and uncertainty in performance of technologies

- Assessment of multiple process configurations under economic and environmental performance indicators

- Use the simplest models that you need to achieve meaningful results and select promising process configurations.

- Use complex models if you need to refine your selection



Thanks for your attention!!

For more information on the Bioenergy Group visit:

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